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SNL, Sigma Off-Gas Team, Contribution to the FY15 DOE/NE-MRWFD Campaign Accomplishments Report

Fuel Cycle Research & Development

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Materials Recovery and Waste Form Development

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Successful Scale Up of Glass Composite Materials (GCM) Iodine Waste Forms (Nenoff, Garino, Rodriguez, Croes, Brady, Mowry, SNL)

This program at Sandia is focused on Iodine waste form development for Fuel Cycle R&D needs. Our research has a general theme of "Capture and Storage of Iodine Fission Gas " in which we are focused on silver loaded zeolite waste forms, evaluation of iodine loaded getter materials (eg., mordenite zeolite), and the development of low temperature glass waste forms that successfully incorporate iodine loaded getter materials from I_2, organic iodide, etc. containing off-gas streams.

For this level 2 milestone, we completed the fabrication of two scaled up Glass Composite Material (GCM) waste forms containing AgI-MOR. One contained methyl iodide-loaded AgI-MOR that was received from Idaho National Laboratory (INL, Test 5, Beds 1 – 3) and the other contained iodine vapor loaded AgI- MOR that was received from Oak Ridge National Laboratory (ORNL, SHB 2/9/15); see figure 1. The composition for each GCM was 20 wt% AgI-MOR and 80 wt% Ferro EG2922 low sintering temperature glass along with enough added silver flake to prevent any I_2 loss during the firing process. Those silver amounts were 1.2 wt% for the GCM with the INL AgI-MOR and 3 wt% for the GCM contained the ORNL AgI-MOR. The GCMs, nominally 100 g, were first uniaxially pressed to 6.35 cm (2.5 inch) diameter disks then cold isostatically pressed before firing in air to 550°C for 1hr. They were cooled slowly (1°C/min) from the firing temperature to avoid any cracking due to temperature gradients. The final GCMs were ~5 cm in diameter (~2 inches) and were non-porous with densities of ~4.2 g/cm^3. X-ray diffraction indicated that they consisted of the amorphous glass phase with mordenite and AgI, whose presence was confirmed also by x-ray fluorescence. Next steps include further scale up of the GCM to industrial sizes, durability studies on the GCM, optimization of composition and sintering conditions based on variables such as N_2 or He versus Air sintering atmosphere (in N_2 or He environments, additional Ag flake is not as necessary as sintering in air).

Upon the directive and with the written approval from DOE/NE and MRWFD campaign leadership, no durability studies were performed on these large scale GCMs. However, due to the (1) consistency of the procedure in scaling up from small scale to the ~2 inch diameter size GCM, (2) the replication of appearance of the GCMs in larger size, and (3) the complimentary materials characterization results (XRD, XRF and water-drop porosity test) when comparing small and large scale GCMs, we anticipate that these scaled-up GCMs will exhibit the same durability characteristics that were reported earlier for the small versions. As data showed the durability of the small scale GCM and release rates approximated those of established nuclear waste glasses, or analogues such as basaltic glass. This suggests that the Bi–Si–Zn GCM of either size is a viable candidate as a repository iodine waste form. A full accounting of this study can be found in the 2015 M2 report: Garino, et.al., Milestone M2FT-15SN0312041, FCRD-MRWFD-2015-000120.

INL AgI-MOR ORNL AgI-MOR

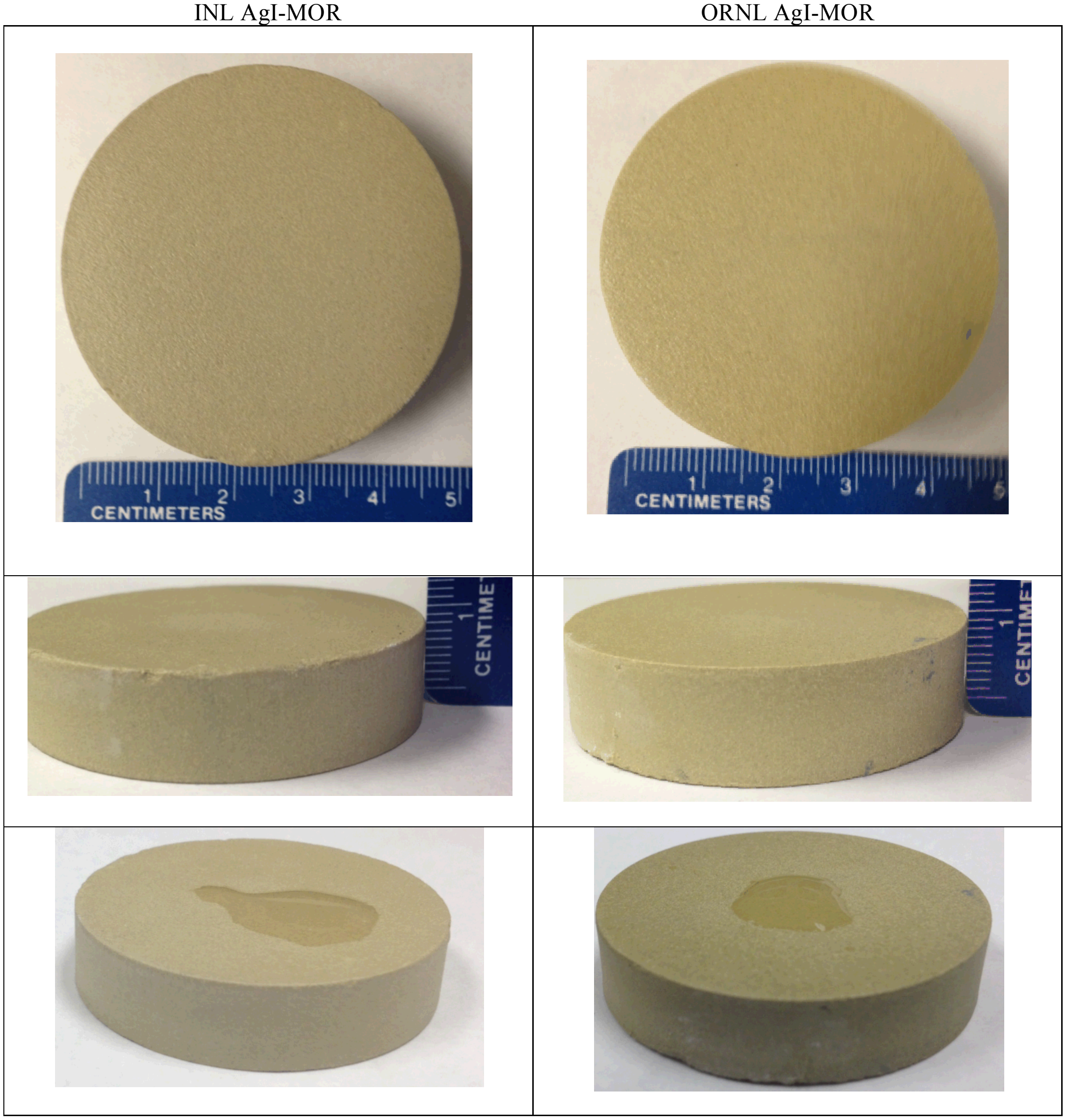

Figure 1: Optical images of the fired GCMs.
(left column) GCM containing 20wt% INL CH_3I-loaed AgI-MOR;
(right column) GCM containing 20 wt% ORNL I_2-loaded AgI-MOR.

Optimization of Silver Addition of CH_3I-MOR encapsulated in GCMs (Nenoff, Garino, Rodriguez, Croes, Brady, Mowry, Coker, SNL)

Sandia-developed low temperature sintering glasses are being examined for the encapsulation of a variety of fission gas loaded getter materials. In particular, we are focusing on the incorporation of silver mordenite iodine capture materials (AgI-MOR) to form Glass Composite Materials (GCMs), for subsequent use as waste forms. The AgI-MOR materials used in this study were methyl iodide loaded Ag-MOR, supplied by INL, Test 5 (Beds 1, 2 and 3). The optimization of Ag flake amounts needed in GCMs was determined for all three materials.

Experiments utilizing simultaneous TGA and DSC with MS off-gas analysis found that for Bed 1, 1.10 wt% of additional Ag flake must be added to the GCM (with 20 wt% AgI-MOR and 80 wt% glass) to suppress iodine loss during sintering (when processing in air) by heating at 5°C/min to 550°C for 1 hr. The amounts for Beds 2 and 3 are 1.15 and 1.20 % Ag, respectively. See figure 2. These amounts are slightly higher than the amounts predicted from the mass loss of iodine when the AgI-MORs are heated alone in air. These results indicate one of two things: (1) a portion of both the added Ag flake and the excess crystalline surface Ag are being oxidized to Ag^+ and migrating into the MOR pores facilitated by the presence of oxygen during heating, and/or (2) the excess Ag is being oxidized to AgO, a non-iodine-reactive nanoparticle both inside MOR pores or on bulk surface.

In contrast, when the GCM is sintered in inert atmosphere these initially present unreacted Ag particles do not re-oxidize to the same extent as when the GCM is sintered in air. Therefore, much of the Ag metal is able to react with the desorbing iodine vapor to form AgI. As a result, a GCM sintered in inert atmosphere requires a much lower amount of Ag flake to suppress iodine loss than when air sintered.

This study also showed that the densification process in the formation of the GCM (in air, where Ag flake addition is necessary) results in the trapping of a small amount of the iodine. This means that less Ag flake addition is required in the GCM waste form than if the glass were not present. Both of these results are similar to what we found previously for I_2 loaded AgI-MOR.

A full accounting of this study can be found in the 2015 M3 report: Garino, et.al., Milestone M3FT-15SN0312043, FCRD-MRWFD-2015-000505.

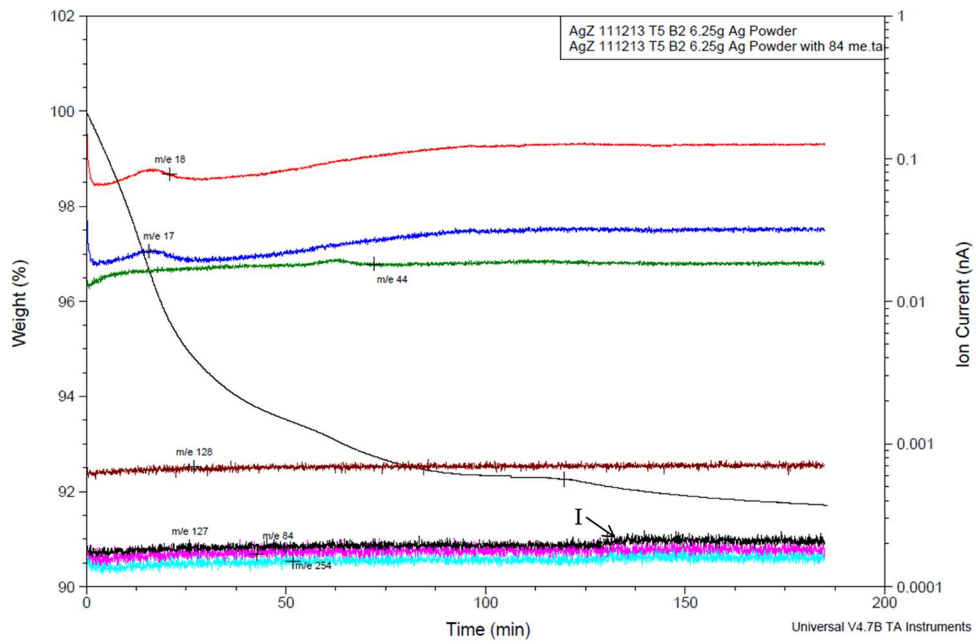

Figure 2. TGA with off-gas MS for as-received ground INL Test 5 Bed 2 AgI-MOR with 6.25 wt% of added Ag flake as a function of time during a heating cycle in air of 5°C/min to 550°C followed by a 1 hr hold. No Iodine loss at GCM sintering temperature cycle.